Microelectrochemical, Crystallographic and Metallurgical Aspects of Corrosion of Ti

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Microscopic aspects of corrosion are of great importance for microsystems, micromaterials, and even for localized corrosion of macroscopic work pieces. Due to the progress in various fields of chemistry, physics, and electronic equipment, investigations in microscopic and molecular dimensions are now available /1, 2/. Therefore, micro-electrochemical and crystallographic investigations can clarify the initiation of pitting, the role of microscopic inhomogeneities, corrosion processes at grain boundaries and finally the corrosion of microsystems which are locally protected by thin films.

Microelectrochemical techniques Great progress of microelectrochemistry was achieved by construction of ultramicro electrodes for amperometric or potentiometric measurements. Combining microscopic observation of materials with mechanic positioners in the mm range or with piezodrives in the nm range, it is possible to approach local defects by microelectrodes measuring local concentrations or potential drops. For some systems, a local resolution in the m range is possible. For special investigations, it is necessary to localize the electrochemical process. This can be done by photoresist techniques, the droplet cell or small capillaries touching only microscopic areas of the material.

Crystallographic structure of grains from EBSD In the case of Ti it has been shown that the crystallographic orientation of the grains has a great influence on corrosion, passivation and catalytic properties /3-5/. The first quantitative correlation was based on Anisotropy Micro Ellipsometry AME which yields film thicknesses and one Euler angle and therefore, a rough idea of grain orientation /4/. The local resolution was limited, however, to 100 m. Electron Back Scattering Diffraction EBSD now allows crystallographic imaging of the polycrystalline material and the determination of 3 Euler angles.

Results for Ti: influence of metallurgy For technical Ti samples, the results of AME, and EBSD agree, but EBSD gives the best results with highest resolution. A comparison with microscopic pictures of anodized electrodes shows that microscopic pictures can

be used to determine at least 2 Euler angles. An analysis of grains, twins and grain boundaries of technical samples shows the influence of metallurgical processes on the surface structure which has a great influence on stability of technical electrodes.

Semiconducting properties of the passive film on Ti and grain orientation Using the photoresist method for preparation of ultramicroelectrodes on Ti, potentiodynamic measurements were carried out in dependence on the crystallographic orientation. They were supported by capacity measurements. It can be shown that close packed planes (0001) are passivated by thin films which are highly doped. Therefore, they have a better corrosion stability than planes with a lower packing density covered by thicker, less doped films. Moreover, the rate of electron transfer reactions is enhanced. Crystallinity and epitaxy of passive films depend on the substrate and the grain orientation as well. Thin passive films on Ti are amorphous, while the oxide films on Zr are crystalline with exception of (0001). /5/

Photocorrosion and photoelectrochemical reactions The corrosion stability of Ti is of great interest for the final deposition of nuclear waste. The influence of radiation on the stability of passive films can be simulated by laser irradiation. Thin, highly doped films on (0001) are more stable than those formed on Ti surfaces with lower packing density. The influence of grain boundaries can be demonstrated by laser induced cathodic deposition of metals.

References: /1/ J.W. Schultze (Ed.): Electrochemical Microsystem Technologies. Electrochimica Acta 42, issue 20-22 (1997) /2/ J.W. Schultze, V. Tsakova, Electrochimica Acta 44 (1999) 3605 /3/ D.G. Wiesler, M.F. Toney, O.R. Melroy, C.S. McMillan, W.H. Smyrl, Surf. Sci. 302 (1994) 341 /4/ S. Kudelka, A. Michaelis, J.W. Schultze, Electrochimica Acta 41 (1996) 863 /5/ J.W. Schultze, M. Schweinsberg, Electrochimica Acta 43 (1998) 2761